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(54) Polymerization of bicyclic amide acetals and polyisocyanates in the presence of moisture.

(57) A process for the preparation of novel polymeric products which involves the reaction of mixtures of bicyclic amide acetals and polyisocyanates with moisture is described.

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POLYMERIZATION OF BICYCLIC AMIDE ACETALS  
AND POLYISOCYANATES IN THE PRESENCE OF MOISTURE

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10 Bicyclic amide acetals and their manufacture are  
described in Synthesis, 1971, page 16 et seqq..

This invention relates to the process for the  
preparation of useful polymers by reaction of bicyclic  
amide acetals and polyisocyanates in the presence of  
15 moisture and to the novel polymer products.

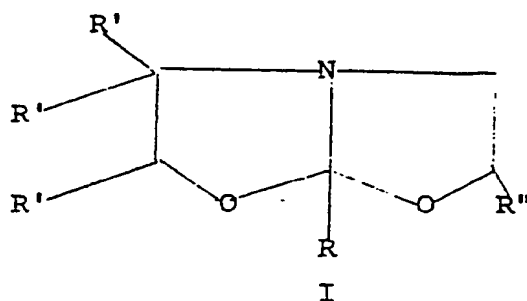
Bicyclic amide acetals have been hydrolyzed with  
an excess of water in Ann. Chem. 716, 135(1968). The  
use of mixtures of bicyclic amide acetals and  
polyisocyanates in moisture-cure systems has not been  
20 described previously.

It has been discovered that mixtures of bicyclic amide  
acetals and polyisocyanates will polymerize in the  
presence of moisture to produce valuable polymers  
useful as coatings, adhesives, and the like. The  
25 polymerization which occurs in this process is  
particularly advantageous in that no volatile materials  
are produced during the polymerization reaction so that  
under normal conditions no foaming or bubble formation  
occurs. This is highly desirable in the case in which  
30 my polymerization process is used to produce coatings.

The bicyclic amide acetals useful in the process of  
this invention are those which conform to the formula  
(I).

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wherein R is a hydrocarbon group having from 1 to 18 carbon atoms and preferably an alkyl group having from 1 to 18 carbon atoms or an aryl or alkaryl group having from 6 to 12 carbon atoms; R' can be independently selected and represents hydrogen, a hydrocarbon group having from 1 to 18 carbon atoms or an ether group having from 2 to 18 carbon atoms; and R'' represents hydrogen, a hydrocarbon group having from 1 to 18 carbon atoms, and an ether group having from 2 to 18 carbon atoms.

The polyisocyanates useful in the process of the invention are those isocyanate compounds which contain at least two isocyanate groups per molecule and included in this group are monomeric, oligomeric and polymeric isocyanate compounds which comply with the foregoing requirement. Polyisocyanates useful in this invention are organic isocyanates having at least two isocyanate groups per molecule. The polyisocyanates can be of low, high or intermediate molecular weight and can be any of a wide variety of organic polyisocyanates including ethylene diisocyanate, trimethylene diisocyanate, dodecamethylene diisocyanate, hexamethylene diisocyanate, hexamethylene diisocyanate trimer, tetraethylene diisocyanate, pentamethylene diisocyanate, propylene-1,2-diisocyanate, 2,3-dimethyl tetramethylene diisocyanate, butylene-1,2-diisocyanate,

butylene-1,3-diisocyanate, 1,4-diisocyanato  
cyclohexane, cyclopentane 1,3-diisocyanate, p-phenylene  
diisocyanate, 1-methyl phenylene-2,4-diisocyanate,  
naphthalene-1,4-diisocyanate, toluene diisocyanate,  
5 diphenyl-4,4'-diisocyanate,  
benzene-1,2,4-triisocyanate, xylylene-1,4-diisocyanate,  
xylylene-1,3-diisocyanate, 4,4'-diphenylene methane  
diisocyanate, 4,4'-diphenylene propane diisocyanate,  
1,2,3,4-tetraisocyanato butane,  
10 butane-1,2,3-triisocyanate, polymethylene polyphenyl  
isocyanate, and other polyisocyanates having an  
isocyanate functionality of at least two as more fully  
disclosed in U.S. Patent Nos. 3,350,362 and 3,382,215.  
Polyisocyanates which are polymeric in nature including  
15 isocyanate prepolymers of all types are included in  
this invention.

The process of this invention can be carried out  
at or about room temperature or above, if desired,  
usually for relatively short reaction times.

20 Although a catalyst is not required in the process  
of this invention, it is sometimes desirable to use a  
catalyst such as an amine, an amino alcohol, a metal  
salt such as dibutyl tin dilaurate, stannous octoate,  
and the like.

25 The amount of moisture required for the  
polymerization reaction of this invention can vary from  
just a trace to an equal molar amount in respect to the  
bicyclic amide acetal used in the process.

Although the exact mechanism whereby the reaction  
30 involved in the process of this invention is not known  
with any degree of certainty, it is possible that the  
bicyclic amide acetal reacts with moisture to form the  
corresponding amide diol  $[\text{HOCH}_2\text{CH}_2\text{N}(\text{COR})\text{CH}_2\text{CH}(\text{R}')\text{OH}]$ ,  
wherein R and R' have the foregoing designations which  
35 amide diol then reacts with the isocyanate groups to  
form the novel polymeric polyamide-polyurethane

materials of this invention. The amide diol itself may possibly act as a promoter in the polymerization reaction of this process.

The invention is further illustrated in the following examples.

#### EXAMPLE 1

A mixture of 4.3g of a bicyclic amide acetal (Formula I,  $R=-CH_2CH_3$ ,  $R'=-H$ ,  $R''=-CH_2OCH_2CH=CH_2$ ) and 8.4g of hexamethylene diisocyanate trimer was applied to a clean glass plate as a 1 mil thick film. The film was allowed to stand at room temperature in the open atmosphere for two days during which it cured to give a clear, colorless film. The following tests were performed.

Mars (Scratch test with fingernail)	-	Slightly
Ribbons (Non-brittleness)	-	Yes
MEK Rubs (Number of rubs before film is attacked)	-	105

#### Solvent tests:

$H_2O$	-	Pass (Does not dissolve in 24 hrs.)
5%NaOH	-	Pass (Does not dissolve in 24 hrs.)
Xylene	-	Pass (Does not dissolve in 24 hrs.)
10%H <sub>2</sub> SO <sub>4</sub>	-	Slight Bubbling on Exposure

#### EXAMPLE 2

The procedure of Example 1 was repeated except that one drop of dibutyltin dilaurate was added to the mixture prior to applying it to the glass plate. The resulting film was found to cure within 5 hours and tests on the film showed results similar to those of Example 1.

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EXAMPLE 3

5 The procedure of Example 2 was repeated except that R" in Formula I was  $-C_6H_5$ . Results similar to those in Example 2 were obtained.

EXAMPLE 4

10 The procedure of Example 1 was followed using 2.15g of the bicyclic amide acetal, 7.30g of a mixture of toluene diisocyanate and hexamethylene diisocyanate trimer and a drop of a tertiary amine catalyst in the mixture. A film of 2 mils thickness was applied to a  
15 clean glass plate and overnight cure at room temperature in the open atmosphere produced a tough film which was not affected by exposure to methyl ethyl ketone, toluene, water or 5% aqueous NaOH.

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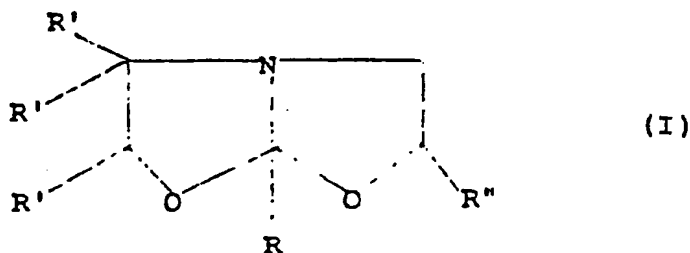
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Patent Claims

1. A cured polymeric material obtained by mixing a bicyclic amide acetal conforming to formula (I):



wherein R is a hydrocarbon group having from 1 to 18 carbon atoms and R' can be independently selected and represents hydrogen, a hydrocarbon group having from 1 to 18 carbon atoms or an ether group having from 2 to 18 carbon atoms; and R'' represents hydrogen, a hydrocarbon group having from 1 to 18 carbon atoms or an ether group having from 2 to 18 carbon atoms, with a polyisocyanate compound having at least two isocyanate groups per molecule and allowing the resulting mixture to react in the presence of moisture.

2. A process for producing the cured polymeric material according to Claim 1, characterized in that a bicyclic amide acetal of formula I is mixed with a polyisocyanate compound having at least two isocyanate groups per molecule and the resulting mixture is allowed to react in the presence of moisture.

3. The process of Claim 2 carried out at or about room temperature or above.

4. The process of Claim 3 wherein the moisture is present in from just a trace up to an equal molar amount based on the moles of bicyclic amide acetal present.

5. The process of Claim 4 wherein there is also included a catalyst.

1        6. The process of Claim 4 wherein R is  $-\text{CH}_2\text{CH}_3$   
and R' is  $-\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$

      7. The process of Claim 4 wherein R is  $-\text{CH}_2\text{CH}_3$   
and R' is  $-\text{C}_6\text{H}_5$ .

5        8. The process of Claim 5 wherein the catalyst is  
a tertiary amine.

      9. The process of Claim 5 wherein the catalyst is  
dibutyl tin dilaurate.

10       10. The process of Claim 4 wherein the  
polyisocyanate is hexamethylene diisocyanate trimer.

      11. The process of Claim 4 wherein the  
polyisocyanate is a mixture of toluene diisocyanate and  
hexamethylene diisocyanate trimer.

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## EUROPEAN PATENT APPLICATION

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③① Priority: **09.10.84 US 658969**

⑦① Applicant: **Ashland Oil, Inc., 1401 Winchester Avenue,  
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④③ Date of publication of application: **14.05.86**  
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⑧⑧ Date of deferred publication of search  
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⑤④ **Polymerization of bicyclic amide acetals and polyisocyanates in the presence of moisture.**

⑤⑦ A process for the preparation of novel polymeric products which involves the reaction of mixtures of bicyclic amide acetals and polyisocyanates with moisture is described.

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# EUROPEAN SEARCH REPORT

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Application number

EP 85 11 2632

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	DE-A-3 235 933 (BAYER) * Page 8, line 11 - page 9, line 19; page 14, example *	1-3	C 08 G 18/38 C 08 G 18/00
P,X	US-A-4 540 767 (A.B. GOEL et al.) * Claim 1; column 2, lines 43-66 *	1-3	
A	US-A-3 637 540 (P. WOLFF et al.)		
A	US-A-4 374 222 (L.W. MEYER)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 G C 07 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-02-1986	Examiner VAN PUymbROECK M.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	